

those of nickel are much less so. The order of relative stabilities appears to be: $\text{UO}_2 > \text{Be} > \text{Ni} > \text{Mn}$. The position of zinc in this series depends upon the ligand. Unfortunately, data are not available for the copper chelates because of their general insolubility. However, titration data indicate that the copper chelate of III is more stable than the uranyl derivative.¹⁴

In general, there is a good correlation between $\log K_{\text{ave}}$, $1/2(\log K_1 + \log K_2)$, for a given metal and the pK_D of the mercaptoacetamides (Fig. 1). A similar relationship is observed using $\log K_1$ or $\log K_2$ instead of $\log K_{\text{ave}}$. This observation has been made for other ligands including β -diketones,¹¹ tropolones¹⁵ and salicylaldehydes.¹⁶

The relationship depicted in Fig. 1 indicates that steric effects are of minor importance in determin-

(14) The value of $\log K^2$ for the copper chelate is estimated to be about 12. Presumably, $\log K_1$ is greater.

(15) B. E. Bryant and W. C. Fernelius, *THIS JOURNAL*, **76**, 1696 (1954).

(16) M. Calvin and K. W. Wilson, *ibid.*, **67**, 2003 (1945).

ing the stabilities of the uranyl, beryllium and (generally) nickel chelates. A steric effect may be involved with the nickel derivative of VI. This chelate is markedly less stable than would be predicted from the $\log K-pK_D$ relationship. The deviation is genuine since the value in question is reproducible. The effect is reminiscent of the reduced stability which results when β -diketones are substituted in the methylene position^{16,17} and may well stem from a common cause. Steric factors may be responsible for the poor $\log K-pK_D$ correlation of zinc chelates. This view is supported by the lessened stability of the 2,6-diethylphenyl derivative (V) relative to that of the unsubstituted compound (I).

Acknowledgments.—This investigation was conducted during the tenure of a Summer Faculty Fellowship for which the author expresses his gratitude to the University of Illinois Research Board. The author is indebted to the Ethyl Corporation for supplying the 2,6-diethylaniline used in the preparation of V.

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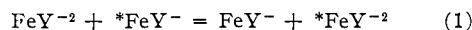
The Exchange of Iron between the Aquo Ferrous and Ferric Versenate Ions

BY W. L. REYNOLDS, NORA LIU AND J. MICKUS

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Electron transfer in the ferrous Versenate–ferric Versenate exchange reaction occurs chiefly between the Versenate complexes of Fe(II) and Fe(III) and not between any dissociation products of these complexes at pH 2. The electron transfer between the undissociated Versenate complexes of Fe(II) and Fe(III) probably occurs by tunnelling. The exchange of ⁵⁹Fe between $\text{Fe}^{+2}(\text{aq})$ and FeY^- was found to be slow, and this exchange was compared with other electron-transfer reactions involving $\text{Fe}^{+2}(\text{aq})$ and ionic oxidants on the basis of Marcus' theory of electron-transfer reactions.

The rate of the electron-transfer reaction between ferrous Versenate and ferric Versenate complexes, or their protonated forms, has been reported¹ to be immeasurably rapid under the experimental conditions employed. At pH 2, the acidity employed by Adamson and Vorres,¹ one must consider the presence of the protonated species HFeY^- and HFeY ,² as well as FeY^{-2} and FeY^- . Here Y^{-4} represents the ethylenediaminetetraacetic acid anion. Three general mechanisms have to be considered for this exchange. The first is the direct electron-transfer reaction 1 between FeY^{-2} and FeY^- or an analogous reaction involving one or more protonated species

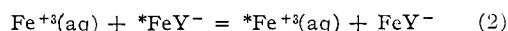


The second mechanism involves the dissociation of the Versenate complexes, an electron-transfer reaction between the aquo ions and reformation of the complexes. This mechanism can be immediately discounted for the following two reasons. First, the formation constants of these complexes are sufficiently large² so that the equilibrium concentrations of $\text{Fe}^{+2}(\text{aq})$ and $\text{Fe}^{+3}(\text{aq})$, and hence

(1) A. W. Adamson and K. S. Vorres, *J. Inorg. Nuclear Chem.*, **3**, 206 (1956).

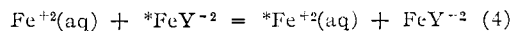
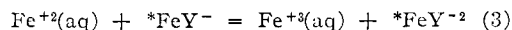
(2) G. Schwarzenbach and J. Heller, *Helv. Chim. Acta*, **34**, 576 (1951).

the rate of exchange between these ions, would be too small to account for the rapid rate of the exchange observed between the Versenate complexes of Fe(II) and Fe(III). Second, Jones and Long³ have measured the rate of the exchange in (2) as



a function of pH. The fact that the exchange is slow means that the dissociation of FeY^- is at least as slow under the same conditions. Hence the dissociation of FeY^- is too slow to be part of the mechanism by which exchange of iron occurs between the Versenate complexes.

The third mechanism to be considered is



This mechanism involves an electron-transfer reaction in (3) and an exchange without electron transfer in (4). Jones and Long³ found that the exchange in (4) was too rapid to measure in the pH range from 1.50 to 4.74. Adamson and Vorres¹ used an excess of Fe^{+2} over Y^{-4} so that aquo Fe^{+2} was present. Hence if the rate constant of the forward reaction in (3) was not too small, re-

(3) S. S. Jones and F. A. Long, *J. Phys. Chem.*, **56**, 25 (1952)

actions 3 and 4 could have provided the observed exchange of radioactive iron between FeY^{-2} and FeY^- . The standard free energy change, ΔF° , of reaction 3 is approximately 15 kcal., so that the free energy of activation would have to be at least this large and the rate constant for (3) would have an upper limit of $100 \text{ (mole/l.)}^{-1} \text{ sec.}^{-1}$. This value of the rate constant for (3) is sufficiently large to account for the exchange observed by Adamson and Vorres.¹ It was therefore decided to make a brief investigation of the rate of exchange of radioactive ^{59}Fe between $\text{Fe}^{+2}(\text{aq})$ and $^*\text{FeY}^-$ in order to determine whether the third mechanism could be eliminated or not.

Experimental

Reagents.—Solutions of $\text{Fe}^{+2}(\text{aq})$ were prepared from reagent grade $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ in the preliminary work and from reagent grade $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in the rate measurements. Solutions of $\text{Na}_2\text{H}_2\text{Y} \cdot 2\text{H}_2\text{O}$ were used to furnish the Versenate ion for complexing of $\text{Fe}(\text{III})$; these are hereafter referred to as EDTA solutions.

Radioactive $^{59}\text{FeCl}_3$ was obtained from Oak Ridge National Laboratory, diluted with inactive FeCl_3 and purified by isopropyl ether extraction.⁴ The $^*\text{Fe}(\text{III})$ was freed of Cl^- by precipitating hydrous ferric oxide, washing and dissolving the precipitate in perchloric acid and repeating this cycle of operations until a negative test for Cl^- was obtained in the wash water. The Cl^- -free oxide then was dissolved in perchloric acid and the resulting $\text{Fe}(\text{III})$ solution was standardized by reducing $\text{Fe}(\text{III})$ to $\text{Fe}(\text{II})$, complexing the $\text{Fe}(\text{II})$ with 1,10-phenanthroline and measuring the absorbance of the latter solution.⁵ Aliquots of this $^*\text{Fe}(\text{III})$ solution were mixed with aliquots of the EDTA solution to give solutions of $^*\text{FeY}^-$ with either Fe^{+3} or EDTA in excess. The concentration of FeY^- in each solution was determined spectrophotometrically at $256 \text{ m}\mu$ with a Beckman DU spectrophotometer.

Procedure.—In preliminary experiments 10.00 ml. of $6.44 \times 10^{-3} M$ $^*\text{Fe}(\text{III})$ solution, $p\text{H}$ adjusted to 2.4 with HCl and containing an excess of $\text{Fe}^{+3}(\text{aq})$ or Y^{-4} , was quickly mixed at room temperature with 10.00 ml. of $6.44 \times 10^{-3} M$ $\text{Fe}^{+2}(\text{aq})$ solution of the same $p\text{H}$. The mixture was permitted to stand for ten seconds, then 1 ml. of $0.095 M$ Br_2 solution was added to oxidize $\text{Fe}^{+2}(\text{aq})$ to $\text{Fe}^{+3}(\text{aq})$ (and FeY^{-2} to FeY^- if FeY^{-2} was present). The oxidations of $\text{Fe}^{+2}(\text{aq})$ to $\text{Fe}^{+3}(\text{aq})$ stopped the exchange between $\text{Fe}^{+2}(\text{aq})$ and $^*\text{FeY}^-$ because the exchange (2) between $\text{Fe}^{+3}(\text{aq})$ and $^*\text{FeY}^-$ proceeds slowly. Next 0.250 g. of Filter-cel was added and 2 ml. of $1 M$ $\text{NH}_3 + 1 M$ NH_4Cl buffer to precipitate hydrous ferric oxide. The precipitate was filtered, with the standard glass chimney apparatus, washed thrice with 5-ml. portions of dilute buffer, twice with 5-ml. portions of absolute alcohol and air dried. The radioactivity of the precipitate was counted using an end-window Geiger-Müller tube and Nuclear-Chicago Model 186 decade scaler. The percentage exchange was read from a calibration curve.

It was established that oxidation of $\text{Fe}^{+2}(\text{aq})$ to $\text{Fe}^{+3}(\text{aq})$ by Br_2 -water and that precipitation of hydrous ferric oxide by $\text{NH}_4\text{Cl} + \text{NH}_3$ buffer did not induce exchange with $^*\text{FeY}^-$. Also when a 0.025 g. quantity of Filter-cel was mixed with $^*\text{FeY}^-$, stirred, filtered and washed, it did not retain any significant radioactivity above the background count showing that FeY^- was not adsorbed on the Filter-cel.

In quantitative experiments on the rate of exchange between $\text{Fe}^{+2}(\text{aq})$ and FeY^- , solutions of $^*\text{Fe}(\text{ClO}_4)_3$ and $\text{Na}_2\text{H}_2\text{Y}$ were mixed to give a solution of $^*\text{FeY}^-$ containing a small excess of $\text{Na}_2\text{H}_2\text{Y}$. This solution was diluted with perchloric acid of the desired acidity and thermostated at $30.3 \pm 1^\circ$. Approximately five minutes before the reaction was to be started an aliquot of non-radioactive $\text{Fe}^{+3}(\text{aq})$ was added so as to complex all Y^{-4} present and leave a small excess of non-radioactive $\text{Fe}^{+3}(\text{aq})$. This procedure put all

$^*\text{Fe}$ initially in the form of $^*\text{FeY}^-$, removed the excess of Y^{-4} so that FeY^{-2} was not formed and gave an excess of $\text{Fe}^{+3}(\text{aq})$ to repress the dissociation of FeY^- . As a result the zero-time exchange was very small or zero. An aliquot of $\text{Fe}(\text{ClO}_4)_2$ solution, at 30.3° , was added to start the exchange and the reaction mixture was diluted to 50.00 ml. with a small amount of the perchloric acid solution also kept at 30.3° . Samples of reaction mixture were withdrawn at various times, treated as described above and the radioactivity of the precipitates determined.

Results

Spectrum of FeY^- .—The absorbance of a $9.61 \times 10^{-5} M$ FeY^- solution, $p\text{H}$ 3.7, containing a fifty-fold excess of EDTA was measured at various wave lengths with a Beckman DU spectrophotometer. A previous report⁶ on the spectrophotometric determination of FeY^- does not state the position of the absorption maximum but does show that the extinction coefficient was virtually independent of $p\text{H}$ over the range 0.8 to 5.0 and that the absorbance of FeY^- is independent of the amount of excess EDTA in the regions where EDTA itself does not absorb. The absorbance measurements reported here show that the absorption maximum lies at $256 \text{ m}\mu$. EDTA did not absorb at this wave length but did start to absorb between 245 and 250 $\text{m}\mu$. Molar extinction coefficients, ϵ , at various wave lengths are listed in Table I. A Beer's-law plot for $256 \text{ m}\mu$ over the concentration range from zero to $10^{-4} M$ was linear and gave a value of $(9.42 \pm 0.06) \times 10^3$ for ϵ . Most of the error in ϵ arises from errors in concentration at low concentrations of FeY^- .

TABLE I

$p\text{H}$ 3.7; room temperature; $(\text{FeY}^-) = 0.61 \times 10^{-5} M$;
(EDTA) = $5 \times 10^{-3} M$

λ , $\text{m}\mu$	$\epsilon \times 10^{-3}$ $M^{-1} \text{ cm.}^{-1}$	λ , $\text{m}\mu$	$\epsilon \times 10^{-3}$ $M^{-1} \text{ cm.}^{-1}$	λ , $\text{m}\mu$	$\epsilon \times 10^{-3}$ $M^{-1} \text{ cm.}^{-1}$
390	3.12	330	27.7	270	85.4
380	4.58	320	35.6	260	93.6
370	6.87	310	43.9	255	94.1
360	10.3	300	53.1	250	92.9
350	14.9	290	63.0	245	87.1
340	20.8	280	74.6	240	81.2

Preliminary Experiments.—Since the $^*\text{Fe}^{+3}(\text{aq})$ and EDTA solutions could not be mixed in exactly stoichiometric amounts, it was decided to use an excess of $^*\text{Fe}^{+3}(\text{aq})$ at first and then gradually increase the amount of EDTA until the latter was present in excess. As long as $^*\text{Fe}^{+3}(\text{aq})$ is present in excess over Y^{-4} , the exchange between $\text{Fe}^{+2}(\text{aq})$ and $^*\text{FeY}^-$, when the $\text{Fe}^{+2}(\text{aq})$ and $^*\text{Fe}(\text{III})$ solutions are mixed, should be slow if the equilibrium in (3) is not established rapidly. (It will be recalled that the evidence indicates that the equilibrium in (4) is established rapidly and also that the exchange in (2) is not rapid.) Some radioactivity will appear in the $\text{Fe}(\text{OH})_3$ precipitate, even if the exchange between Fe^{+2} and $^*\text{FeY}^-$ is negligible, as a result of some of the $^*\text{Fe}^{+3}(\text{aq})$ not being complexed by EDTA. However, as the amount of EDTA is increased, the radioactivity in the

(6) W. Nielsch and G. Boltz, *Microchim. Acta*, 481 (1954).

(4) R. W. Dodson, G. J. Forney and E. H. Swift, *THIS JOURNAL*, **58**, 2573 (1936).

(5) W. B. Fortune and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **10**, 60 (1938).

TABLE II

Room temperature *ca.* 28°; pH 2.4 except as noted; total volume = 20 ml.

Expt. no.	EDTA taken, mmole	FeY ⁻ , mmole	Fe ⁺ , mmole	Fe ²⁺ , mmole	FeY ⁻² , mmole	Activity, <i>c/m</i>	Apparent exchange, %	<i>t</i> , sec.
1	0.059	0.059	0.005	0.064	...	621	14	10
2	.061	.061	.003	.064	...	458	10	10
3	.063	.063	.001	.064	...	394	9.0	10
4	.064	.064064	...	353	7.6	10
5	.065	.064063	0.001	3370	82.6	10
6	.080	.064048	0.016	3420	84.0	10
7	.061 ^a	.061	0.003	.064	...	446	10	10

^a pH 2.0 instead of 2.4.

Fe(OH)₃ precipitate will decrease as a result of a decrease in the amount of excess *Fe³⁺(aq). The radioactivity in the precipitate will be a minimum when *Fe³⁺(aq) and EDTA are present in stoichiometric amounts. Whenever EDTA is present in

the apparent per cent exchange, as determined from the activity of the precipitate, will not appear to be as large as it really is but will be less than this by an amount which is dependent upon the excess of EDTA in the *Fe(III) solution.

The results of exchange experiments for various amounts of EDTA present in the reaction mixture are given in Table II. The length of time in seconds between mixing of the Fe²⁺(aq) and *Fe(III) solutions and oxidation of Fe²⁺(aq) is given in the last column. When *Fe³⁺(aq) is present in excess over EDTA, it is seen that the amount of apparent exchange is small and that it decreases as the excess of *Fe³⁺(aq) decreases. For example, in the first three experiments the apparent exchanges are 14, 10 and 9%, whereas the apparent exchanges calculated on the basis of the excess of *Fe³⁺(aq) and the total iron precipitated are 14.5, 9 and 3%. The apparent percentage exchange in the third and fourth experiments is somewhat higher than the exchange calculated on the basis of the uncomplexed *Fe³⁺(aq) present. This might result from the presence of very small amounts of FeY⁻² being present when the excess of Fe³⁺(aq) becomes very small. When sufficient EDTA to form an appreciable amount of FeY⁻² was taken, the apparent percentage exchange became very large, as expected.

Rate Measurements.—The data in Table II showed that the exchange between Fe²⁺(aq) and FeY⁻ was not too rapid to measure. Hence exchange rate measurements were made at various concentrations of H⁺, Fe²⁺(aq), FeY⁻ and Fe³⁺(aq). Figure 1 shows a typical plot of log (1 - F) versus time where F is the observed fraction exchange at time *t*. The slope *S* of the straight line is given by⁷

$$S = -R_0(A + B)/2.30 AB \quad (5)$$

where *R*₀ is the observed rate of exchange and *A* and *B* are the concentrations of the two exchanging species. To obtain *R*, the rate of exchange between Fe²⁺(aq) and FeY⁻, *R*₀ was corrected for the very small rate of exchange between Fe³⁺(aq) and FeY⁻ using the expression given by Jones and Long.³ Because variation of concentration of reactants usually produced a variation of ionic strength *μ* all rates of exchange *R* were corrected to an intermediate value of *μ* (*μ* = 0.100) employ-

(7) R. J. Prestwood and A. C. Wahl, *THIS JOURNAL*, **71**, 3137 (1949).

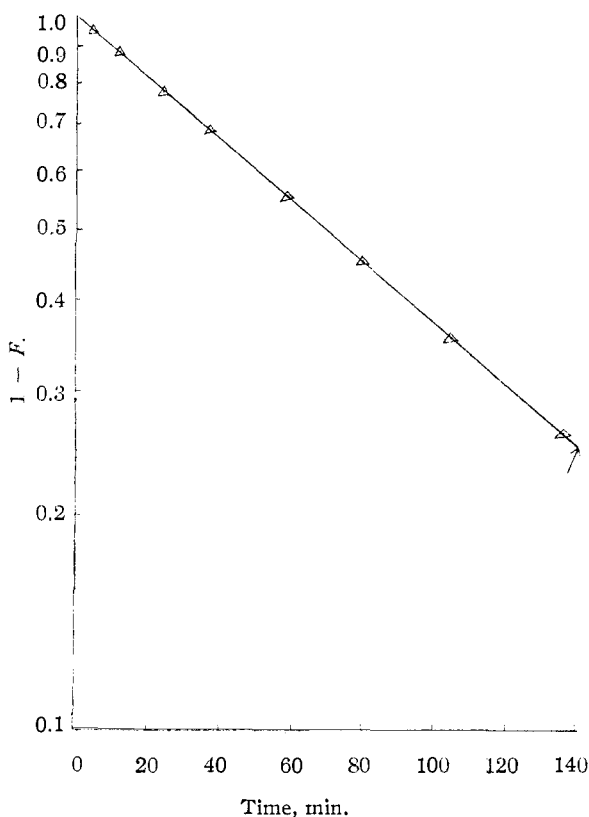


Fig. 1.—Plot of log (1 - F) versus *t* for the Fe²⁺(aq) + *FeY⁻ exchange reaction at 30.3° and *μ* = 0.116; (H⁺) = 0.090 *M*; (Fe²⁺) = 5.85 × 10⁻³ *M*; (FeY⁻) = 1.70 × 10⁻³ *M*; (Fe³⁺) = 3.40 × 10⁻⁴ *M*.

excess over Fe³⁺(aq) in the *Fe solution, some FeY⁻² will be formed when the Fe²⁺(aq) and Fe(III) solutions are mixed. The rapid exchange observed by Adamson and Vorres¹ will then occur between Fe(II) and *FeY⁻. However, all Fe(II) will not be precipitated in this case when the NH₃ + NH₄Cl buffer is added because some of it is complexed, after oxidation of FeY⁻² by Br₂, as FeY⁻. Hence

ing the activity coefficients from Kolthoff and Elving⁸ and the form of the rate law established for the concentration ranges used here.

All data were treated by the method of least squares to give values of R_0 and the orders of reaction with respect to (H^+) , (Fe^{+2}) and (FeY^-) . The data are given in Table III. It is only for

TABLE III

RATES OF EXCHANGE OF ^{59}Fe BETWEEN $Fe^{+3}_{(aq)}$ AND FeY^-
 $30.3 \pm 0.1^{\circ}$; $(Fe^{+3}_{(aq)}) = 3.40 \times 10^{-4} M$

(H^+) M	(Fe^{+2}) $10^2 M$	(FeY^-) $10^2 M$	μ	$R_0 \times 10^6$ $M \text{ min.}^{-1}$	$R_1 \times 10^6$ $M \text{ min.}^{-1}$
0.016	1.18	1.70	0.058	1.26	1.02
.016	1.18	1.70	.058	0.83	0.67
.044	1.18	1.70	.087	6.72	6.35
.044	1.18	1.70	.087	6.30	5.94
.090	1.18	1.70	.134	18.1	20.7
.090	1.18	1.70	.134	16.2	18.0
.20	1.17	1.70	.244	45.1	64.4
.20	1.17	1.70	.244	43.0	61.4
.090	0.585	1.70	.116	10.2	10.7
.090	0.585	1.70	.116	11.6	12.2
.090	2.34	1.70	.168	22.7	28.0
.090	2.34	1.70	.168	25.0	30.8
.090	1.76	1.70	.150	21.9	25.6
.090	2.34	0.850	.160	14.8	18.3
.090	2.34	0.850	.160	10.3	12.7
.090	2.34	1.28	.163	17.6	21.7
.090	2.34	1.28	.163	15.9	19.6

$\mu = 0.244$ that the correction to the observed rate becomes large. However, if the data for this value of μ are omitted, the order of the reaction with respect to (H^+) is not significantly changed. The least squares values and their standard deviations for the order of reaction with respect to (H^+) , $(Fe^{+2}_{(aq)})$ and (FeY^-) are 1.68 ± 0.07 , 0.69 ± 0.05 and 0.93 ± 0.19 , respectively. In one experiment the concentration of $Fe^{+3}_{(aq)}$ was doubled, but the value of R remained unchanged within the experimental error of $\pm 8\%$. Therefore over the concentration ranges employed the rate of exchange between $Fe^{+2}_{(aq)}$ and FeY^- can be represented by the empirical expression

$$R = k(H^+)^{1.7}(Fe^{+2})^{0.7}(FeY^-) \quad (6)$$

The fractional powers in (6) may mean that more than one term is involved in the rate expression and that, for example, $(Fe^{+2})^0$ is involved in one term and (Fe^{+2}) is involved in another. The first power of (FeY^-) would indicate that (FeY^-) occurs in every term. In order to reliably decompose (6) into a number of separate terms, it would be necessary to study the variation of R over larger concentration ranges. The concentration ranges would mainly have to be extended in the direction of higher concentrations. If (Fe^{+2}) is made too small the correction of R_0 for the exchange between $Fe^{+3}_{(aq)}$ and FeY^- becomes too large to give accurate results; if (H^+) is made too small precipitation of

$Fe^{+3}_{(aq)}$ will begin. In order to attain higher concentrations, the exchange will have to be studied at a much higher ionic strength using $NaClO_4$, for example, to maintain μ constant while varying concentrations of reactants over the larger concentration ranges.

The effect of temperature on reaction rate was not determined. Since k in (6) is an unknown function of several rate and/or equilibrium constants, the activation energy corresponding to k would also be an unknown function of various heats of activation and/or reaction and would not be particularly useful.

Discussion

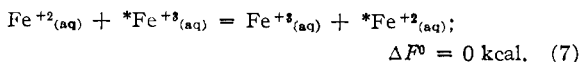
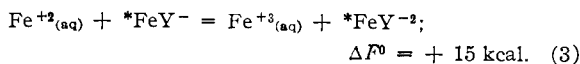
At pH 2.0 and $\mu = 0.1$, where the average rate of exchange between $Fe^{+2}_{(aq)}$ and FeY^- was 4.7×10^{-7} (mole/l.) min.^{-1} for $(Fe^{+2}) = 1.18 \times 10^{-2} M$ and $(FeY^-) = 1.70 \times 10^{-2} M$, any second order rate constant, k_2 , for exchange by a path involving $Fe^{+2}_{(aq)}$ and any ferric Versenate species obeys the relation

$$k_2 \leq 4.0 \times 10^{-4} \text{ (mole/l.)}^{-1} \text{ sec.}^{-1}$$

The upper limit for k_2 is a factor of 10^{-5} – 10^{-6} too small to account for exchange between FeY^{-2} and FeY^- by reactions 3 and 4. Therefore, it is concluded, the rapid exchange between FeY^{-2} and FeY^- noted by Adamson and Vorres¹ occurred between ferrous Versenate and ferric Versenate species.

Both of the reactions 1 and 3 involve electron transfer between spin-free complexes. The very small rate of reaction 3, as compared to reaction 1, is most probably the result of Franck-Condon restrictions requiring a considerable activation energy in (3) as compared to (1) in addition to the over-all free energy change in (3) of approximately 15 kcal. mole^{-1} . Since the exchange reaction 1 is rapid, solvent and ligand reorientation in $*FeY^-$, before conversion to $*FeY^{-2}$, requires only a small free energy change at most. On the other hand, the free energy of activation of the $Fe^{+2}_{(aq)} + Fe^{+3}_{(aq)}$ exchange⁹ is approximately 17 kcal. mole^{-1} at 30° of which a considerable fraction may be attributed to the reorientation process¹⁰ in forming the transition state. It seems probable that it is this free energy for reorienting ligand and solvent water molecules around Fe^{+2} , preparatory to charge transfer, in addition to the over-all free energy of reaction of 15 kcal. which makes the rate constant for (3) less than 4.0×10^{-4} (mole/l.) $^{-1}$ sec.^{-1} .

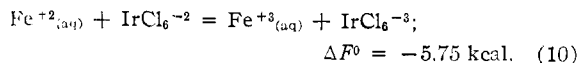
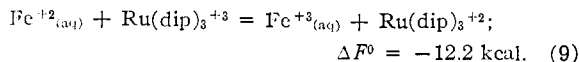
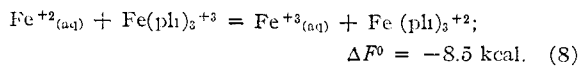
It is interesting to compare reaction 3 with reactions 7, 8, 9 and 10. In (8) and (9) "ph" and



(9) J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952).

(8) I. M. Kolthoff and P. J. Elving, "Treatise on Analytical Chemistry," Vol. I, Part 1, The Interscience Encyclopedia, Inc., New York, N. Y., p. 240, 242, 243.

(10) (a) R. A. Marcus, *Discussions Faraday Soc.*, April 1960, preprint. (b) R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956); **26**, 867 (1957).



"dip" refer to 1,10-phenanthroline and α, α' -dipyridyl, respectively. The rate constant for (7) is approximately $4(\text{mole/l.})^{-1} \text{ sec.}^{-1}$ and those for (8), (9) and (10) are greater than $10^5(\text{mole/l.})^{-1} \text{ sec.}^{-1}$ at 25° . If it is assumed that electron tunnelling occurs when the reactants approach to such a distance that the first coordination shells are in contact and that reorientation of the first coordination shells is unnecessary, then equations 11 and 12 relating the free energy of activation, ΔF^* , and the over-all standard free energy change, ΔF^0 , of the reaction may be employed.

$$\Delta F^* = \frac{z_1^* z_2^* e^2}{RD_s} + m^2 (\Delta z)^2 e^2 \left(\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{R} \right) \left(\frac{1}{D_{\text{op}}} - \frac{1}{D_s} \right) \quad (11)$$

$$- (2m + 1)(\Delta z)^2 e^2 \left(\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{R} \right) \left(\frac{1}{D_{\text{op}}} - \frac{1}{D_s} \right) = \Delta F^0 + T\Delta S_e + (z_1 z_2 - z_1^* z_2^*) e^2 \quad (12)$$

where z_1^* and z_2 are the charges on the reactant ions before electron tunnelling, z_1 and z_2 are the charges on the reactant ions after tunnelling, Δz

is equal to $|z_1^* - z_1|$, e is the electronic charge, r_1 and r_2 are the radii of reactant ions 1 and 2, respectively, and each is equal to one-half the diameter of the indicated metal ion plus first coordination shell, R is equal to the sum ($r_1 + r_2$), D_{op} is the optical dielectric constant, D_s is the low-frequency, small-field-strength dielectric constant of the solvent, $T\Delta S_e$ is the free energy change resulting from a change in the number of unpaired electrons and m is a constant determined by (12). The value of r_1 , the radius of $\text{Fe}^{+2}_{(\text{aq})}$, is the same for all reactions listed and is approximately 3.44 \AA . The value of r_2 is approximately 3.44 for (7), 4.4 for (3), 7.08 for (8), 5.92 for (9) and 4.05 \AA for (10). The value of $T\Delta S_e$ is zero for all five reactions.

If the relative rates of these reactions are compared, the theory predicts that the rate constants of (8), (9) and (10) will be greater than that of (7) by at least a factor of 10^4 – 10^5 and this is observed. Also the theory predicts that the rate constant of (7) will be at least 10^2 times greater than that of (3) as observed. However, the values of the calculated rate constants are a factor of 10^5 too large for (7) and a factor of at least 10^7 too large for (3). Application of Marcus' theory for reorientation of inner shell ligands^{10a} may remove this discrepancy; these calculations have not been made yet for this series of reactions.

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Reactions of Amminepentacyanoferrates(II) and (III) with Azide and Thiocyanate

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Aqueous solution of amminepentacyanoferrate(III) in the presence of azide or thiocyanate develops an intense purple or blue color, respectively. The colored complexes are shown to be azidopentacyanoferrate(III) or pentacyanothiocyanatoferrate(III). Tetrabutylammonium salts of these complexes have been crystallized and analyzed. The log ratio method for the exchange reactions of ammonia in aqueous solutions of amminepentacyanoferrate(III) with azide or thiocyanate gives a combining ratio of 1:1. In addition, apparent equilibrium constants for various exchange reactions have been calculated, with an over-all reproducibility of approximately $\pm 5\%$. The calculated equilibrium constants for the exchange reactions of azidopentacyanoferrate(III) with ammonia (K_1), pyridine (K_2), hydroxyl (K_3) are $K_1 - 3.9$, $K_2 - 3.25$, $K_3 - 200$ and the calculated equilibrium constants for pentacyanothiocyanatoferrate(III) with ammonia (K_1), pyridine (K_2) and hydroxyl (K_3) are $K_1 - 29.7$, $K_2 - 24.4$ and $K_3 - 1500$.

Aquo- and amminepentacyanoferrates(II) yield color tests with azide, thiocyanate and a number of organic functional groups, like aromatic amines, aromatic aldehydes, thioaldehydes, hydrazides. These reactions have been recommended by Feigl¹ as suitable spot tests for identification purposes. The reactions of amminepentacyanoferrate(II) with aromatic amines have been described by Herington.²⁻⁴ However, most of these reactions are not understood. In fact, the

purple color for the reaction of azide with amminepentacyanoferrate(II) in presence of an oxidizing agent has been attributed by Baudisch⁵ to the aquopentacyanoferrate(III). In a recent publication Jaselskis and Edwards⁶ suggest that this color definitely is caused by a distinct azide complex; also they observe that thiocyanate reacts in a manner similar to azide. Thus, it seems of interest to investigate not only the reactions of azide and thiocyanate with amminepentacyanoferrate(II) but also with amminepentacyanoferrate(III). Both of these complexes have

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